Molecular Dynamics Simulations of N_2 Clathrate Hydrates

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The ambient pressure N_2 clathrate hydrate has been shown to form structure II. Upon pressurizing N_2 clathrate hydrates, a splitting of the N_2 vibron peak occurs at about 8.5 kbar [1]. This splitting is accompanied by a change in the slope of the H_2O symmetric stretch peak frequency versus pressure. In addition, there are indications from neutron diffraction that a fraction of the large cages are doubly occupied by the N_2 molecules [2].

In order to obtain detailed insight into these phenomena, in particular to investigate the possibility of double occupancy, we have performed molecular dynamics (MD) simulations of the N_2 type II clathrate hydrate. For the simulations, an analysis of the N_2-H_2O potential model has been performed. It turns out that our model is very similar to the potential energy surfaces as calculated in ab initio calculations and is in accord with experimental data.

The simulation cell consisted of 8 unit cells, formed by 1088 water molecules, and thus comprising 64 large and 128 small cavities. We have performed (N,p,T) as well as (N,V,T) calculations. The occupation numbers of these cavities (being either in single or double occupancy) varied in order to investigate the stability and properties of the various mixtures. We have determined various thermodynamic quantities, and in addition investigated the positions and orientations of guest and host molecules. In order to make contact with experimental data, we have determined Raman frequencies of the N_2 molecules within the cages. The influence of applied pressure has been investigated. We have also tested the sensitivity to changes in the force field.

[1] M.G.E. van Hinsberg, M.I.M. Scheerboom, and J.A. Schouten, *J. Chem. Phys*. **99**, 752 (1993).
[2] W.F. Kuhs, B. Chazallon, P.G. Radaelli and F. Pauer, *J. of Incl. Phen. and Molec. Recogn. in Chem*. **29**, 65 (1997).